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(54) Title: PRODUCTION OF OLEFINS (57) Abstract A process for the catalytic cracking of an olefin-rich feedstock which is selective towards light olefins in the effluent, the process comprising contacting a hydrocarbon feedstock containing one or more olefins, with a MFI-type crystalline silicate catalyst having a silicon/aluminium atomic ratio of at least about 300 at an inlet temperature of from 500 to 600 °C, at an olefin partial pressure of from 0.1 to 2 bars and the feedstock being passed over the catalyst at an LHSV of from 10 to 30 h ⁻¹ , to produce an effluent with an olefin content of lower molecular weight than that of the feedstock.		

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PRODUCTION OF OLEFINS

The present invention relates to a process for cracking an olefin-rich hydrocarbon feedstock which is selective towards light olefins in the effluent. In particular, olefinic feedstocks from refineries or petrochemical plants can be converted selectively so as to redistribute the olefin content of the feedstock in the resultant effluent.

It is known in the art to use zeolites to convert long chain paraffins into lighter products, for example in the catalytic dewaxing of petroleum feedstocks. While it is not the objective of dewaxing, at least parts of the paraffinic hydrocarbons are converted into olefins. It is known in such processes to use crystalline silicates for example of the MFI type, the three-letter designation "MFI" representing a particular crystalline silicate structure type as established by the Structure Commission of the International Zeolite Association. Examples of a crystalline silicate of the MFI type are the synthetic zeolite ZSM-5 and silicalite and other MFI type crystalline silicates are known in the art.

GB-A-1323710 discloses a dewaxing process for the removal of straight-chain paraffins and slightly branched-chain paraffins, from hydrocarbon feedstocks utilising a crystalline silicate catalyst, in particular ZSM-5. US-A-4247388 also discloses a method of catalytic hydrodewaxing of petroleum and synthetic hydrocarbon feedstocks using a crystalline silicate of the ZSM-5 type. Similar dewaxing processes are disclosed in US-A-4284529 and US-A-5614079. The catalysts are crystalline aluminosilicates and the above-identified prior art documents disclose the use of a wide range of Si/Al ratios and differing reaction conditions for the disclosed dewaxing processes.

GB-A-2185753 discloses the dewaxing of hydrocarbon feedstocks using a silicalite catalyst. US-A-4394251 discloses

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hydrocarbon conversion with a crystalline silicate particle having an aluminium-containing outer shell.

It is also known in the art to effect selective conversion of hydrocarbon feeds containing straight-chain and/or slightly branched-chain hydrocarbons, in particular paraffins, into a lower molecular weight product mixture containing a significant amount of olefins. The conversion is effected by contacting the feed with a crystalline silicate known as silicalite, as disclosed in GB-A-2075045, US-A-4401555 and US-A-4309276. Silicalite is disclosed in US-A-4061724.

Silicalite catalysts exist having varying silicon/aluminium atomic ratios and different crystalline forms. EP-A-0146524 and 0146525 in the name of Cosden Technology, Inc. disclose crystalline silicas of the silicalite type having monoclinic symmetry and a process for their preparation. These silicates have a silicon to aluminium atomic ratio of greater than 80.

WO-A-97/04871 discloses the treatment of a medium pore zeolite with steam followed by treatment with an acidic solution for improving the butene selectivity of the zeolite in catalytic cracking.

A paper entitled "De-alumination of HZSM-5 zeolites: Effect of steaming on acidity and aromatization activity", de Lucas et al, Applied Catalysis A: General 154 1997 221-240, published by Elsevier Science B.V. discloses the conversion of acetone/n-butanol mixtures to hydrocarbons over such dealuminated zeolites.

It is yet further known, for example from US-A-4171257, to dewax petroleum distillates using a crystalline silicate catalyst such as ZSM-5 to produce a light olefin fraction, for example a C₃ to C₄ olefin fraction. Typically, the reactor temperature reaches around 500°C and the reactor employs a low hydrocarbon partial pressure which favours the conversion of the petroleum distillates into propylene. Dewaxing cracks paraffinic chains

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leading to a decrease in the viscosity of the feedstock distillates, but also yields a minor production of olefins from the cracked paraffins.

EP-A-0305720 discloses the production of gaseous olefins by catalytic conversion of hydrocarbons. EP-B-0347003 discloses a process for the conversion of a hydrocarbonaceous feedstock into light olefins. WO-A-90/11338 discloses a process for the conversion of C_2 - C_{12} paraffinic hydrocarbons to petrochemical feedstocks, in particular to C_2 to C_4 olefins. US-A-5043522 and EP-A-0395345 disclose the production of olefins from paraffins having four or more carbon atoms. EP-A-0511013 discloses the production of olefins from hydrocarbons using a steam activated catalyst containing phosphorous and H-ZSM-5. US-A-4810356 discloses a process for the treatment of gas oils by dewaxing over a silicalite catalyst. GB-A-2156845 discloses the production of isobutylene from propylene or a mixture of hydrocarbons containing propylene. GB-A-2159833 discloses the production of a isobutylene by the catalytic cracking of light distillates.

It is known in the art that for the crystalline silicates exemplified above, long chain olefins tend to crack at a much higher rate than the corresponding long chain paraffins.

It is further known that when crystalline silicates are employed as catalysts for the conversion of paraffins into olefins, such conversion is not stable against time. The conversion rate decreases as the time on stream increases, which is due to formation of coke (carbon) which is deposited on the catalyst.

These known processes are employed to crack heavy paraffinic molecules into lighter molecules. However, when it is desired to produce propylene, not only are the yields low but also the stability of the crystalline silicate catalyst is low. For example, in an FCC unit a typical propylene output is 3.5wt%.

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The propylene output may be increased to up to about 7-8wt% propylene from the FCC unit by introducing the known ZSM-5 catalyst into the FCC unit to "squeeze" out more propylene from the incoming hydrocarbon feedstock being cracked. Not only is this increase in yield quite small, but also the ZSM-5 catalyst has low stability in the FCC unit.

There is an increasing demand for propylene in particular for the manufacture of polypropylene.

The petrochemical industry is presently facing a major squeeze in propylene availability as a result of the growth in propylene derivatives, especially polypropylene. Traditional methods to increase propylene production are not entirely satisfactory. For example, additional naphtha steam cracking units which produce about twice as much ethylene as propylene are an expensive way to yield propylene since the feedstock is valuable and the capital investment is very high. Naphtha is in competition as a feedstock for steam crackers because it is a base for the production of gasoline in the refinery. Propane dehydrogenation gives a high yield of propylene but the feedstock (propane) is only cost effective during limited periods of the year, making the process expensive and limiting the production of propylene. Propylene is obtained from FCC units but at a relatively low yield and increasing the yield has proven to be expensive and limited. Yet another route known as metathesis or disproportionation enables the production of propylene from ethylene and butene. Often, combined with a steam cracker, this technology is expensive since it uses ethylene as a feedstock which is at least as valuable as propylene.

EP-A-0109059 discloses a process for converting olefins having 4 to 12 carbon atoms into propylene. The olefins are contacted with an alumino-silicate having a crystalline and zeolite structure (e.g. ZSM-5 or ZSM-11) and having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio equal to or lower than 300. The specification requires high space velocities of greater than 50kg/h per kg of

pure zeolite in order to achieve high propylene yield. The specification also states that generally the higher the space velocity the lower the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio (called the Z ratio). This specification only exemplifies olefin conversion processes over short periods (e.g. a few hours) and does not address the problem of ensuring that the catalyst is stable over longer periods (e.g. at least 160 hours or a few days) which are required in commercial production. Moreover, the requirement for high space velocities is undesirable for commercial implementation of the olefin conversion process.

Thus there is a need for a high yield propylene production method which can readily be integrated into a refinery or petrochemical plant, taking advantage of feedstocks that are less valuable for the market place (having few alternatives on the market).

On the other hand, crystalline silicates of the MFI type are also well known catalysts for the oligomerisation of olefins. For example, EP-A-0031675 discloses the conversion of olefin-containing mixtures to gasoline over a catalyst such as ZSM-5. As will be apparent to a person skilled in the art, the operating conditions for the oligomerisation reaction differ significantly from those used for cracking. Typically, in the oligomerisation reactor the temperature does not exceed around 400°C and a high pressure favours the oligomerisation reactions.

GB-A-2156844 discloses a process for the isomerisation of olefins over silicalite as a catalyst. US-A-4579989 discloses the conversion of olefins to higher molecular weight hydrocarbons over a silicalite catalyst. US-A-4746762 discloses the upgrading of light olefins to produce hydrocarbons rich in C_5+ liquids over a crystalline silicate catalyst. US-A-5004852 discloses a two-stage process for conversion of olefins to high octane gasoline wherein in the first stage olefins are oligomerised to C_5+ olefins. US-A-5171331 discloses a process for the production of

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gasoline comprising oligomerising a C_2 - C_6 olefin containing feedstock over an intermediate pore size siliceous crystalline molecular sieve catalyst such as silicalite, halogen stabilised silicalite or a zeolite. US-A-4414423 discloses a multistep process for preparing high-boiling hydrocarbons from normally gaseous hydrocarbons, the first step comprising feeding normally gaseous olefins over an intermediate pore size siliceous crystalline molecular sieve catalyst. US-A-4417088 discloses the dimerising and trimerising of high carbon olefins over silicalite. US-A-4417086 discloses an oligomerisation process for olefins over silicalite. GB-A-2106131 and GB-A-2106132 disclose the oligomerisation of olefins over catalysts such as zeolite or silicalite to produce high boiling hydrocarbons. GB-A-2106533 discloses the oligomerisation of gaseous olefins over zeolite or silicalite.

It is an object of the present invention to provide a process for using the less valuable olefins present in refinery and petrochemical plants as a feedstock for a process which, in contrast to the prior art processes referred to above, catalytically converts olefins into lighter olefins, and in particular propylene.

It is another object of the invention to provide a process for producing propylene having a high propylene yield and purity.

It is a further object of the present invention to provide such a process which can produce olefin effluents which are within, at least, a chemical grade quality.

It is yet a further object of the present invention to provide a process for producing olefins having a stable olefinic conversion and a stable product distribution over time.

It is yet a further object of the present invention to provide a process for converting olefinic feedstocks having a high yield on an olefin basis towards propylene, irrespective of

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the origin and composition of the olefinic feedstock.

The present invention provides a process for the catalytic cracking of an olefin-rich feedstock which is selective towards light olefins in the effluent, the process comprising contacting a hydrocarbon feedstock containing one or more olefins, with a MFI-type crystalline silicate catalyst having a silicon/aluminium atomic ratio of at least about 300 at an inlet temperature of from 500 to 600°C, at an olefin partial pressure of from 0.1 to 2 bars and the feedstock being passed over the catalyst at an LHSV of from 10 to 30h⁻¹, to produce an effluent with an olefin content of lower molecular weight than that of the feedstock.

The present invention can thus provide a process wherein olefin-rich hydrocarbon streams (products) from refinery and petrochemical plants are selectively cracked not only into light olefins, but particularly into propylene. The olefin-rich feedstock may be passed over a MFI-type crystalline silicate catalyst with a particular Si/Al atomic ratio of at least about 300. The catalyst is preferably a commercially available catalyst which has been prepared by crystallisation using an organic template and has been unsubjected to any subsequent steaming or de-alumination process. The feedstock may be passed over the catalyst at a temperature ranging between 500 to 600°C, an olefin partial pressure of from 0.1 to 2 bars and an LHSV of from 10 to 30h⁻¹ to yield at least 30 to 50% propylene based on the olefin content in the feedstock.

In this specification, the term "silicon/aluminium atomic ratio" is intended to mean the Si/Al atomic ratio of the overall material, which may be determined by chemical analysis. In particular, for crystalline silicate materials, the stated Si/Al ratios apply not just to the Si/Al framework of the crystalline silicate but rather to the whole material.

The feedstock may be fed either undiluted or diluted with

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an inert gas such as nitrogen. In the latter case, the absolute pressure of the feedstock constitutes the partial pressure of the hydrocarbon feedstock in the inert gas.

The various aspects of the present invention will now be described in greater detail however by example only with reference to the accompanying drawing, in which:-

Figure 1 shows the relationship between the amount of olefin feedstock conversion, the propylene yield, and the sum of the other components and the silicon/aluminium atomic ratio in a catalytic cracking process of the invention.

In accordance with the present invention, cracking of olefins is performed in the sense that olefins in a hydrocarbon stream are cracked into lighter olefins and selectively into propylene. The feedstock and effluent preferably have substantially the same olefin content by weight. Typically, the olefin content of the effluent is within $\pm 15\text{wt}\%$, more preferably $\pm 10\text{wt}\%$, of the olefin content of the feedstock. The feedstock may comprise any kind of olefin-containing hydrocarbon stream. The feedstock may typically comprise from 10 to 100wt% olefins and furthermore may be fed undiluted or diluted by a diluent, the diluent optionally including a non-olefinic hydrocarbon. In particular, the olefin-containing feedstock may be a hydrocarbon mixture containing normal and branched olefins in the carbon range C_4 to C_{10} , more preferably in the carbon range C_4 to C_6 , optionally in a mixture with normal and branched paraffins and/or aromatics in the carbon range C_4 to C_{10} . Typically, the olefin-containing stream has a boiling point of from around -15 to around 180°C .

In particularly preferred embodiments of the present invention, the hydrocarbon feedstocks comprise C_4 mixtures from refineries and steam cracking units. Such steam cracking units crack a wide variety of feedstocks, including ethane, propane, butane, naphtha, gas oil, fuel oil, etc. Most particularly, the

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hydrocarbon feedstock may comprises a C₄ cut from a fluidized-bed catalytic cracking (FCC) unit in a crude oil refinery which is employed for converting heavy oil into gasoline and lighter products. Typically, such a C₄ cut from an FCC unit comprises around 50wt% olefin. Alternatively, the hydrocarbon feedstock may comprise a C₄ cut from a unit within a crude oil refinery for producing methyl tert-butyl ether (MTBE) which is prepared from methanol and isobutene. Again, such a C₄ cut from the MTBE unit typically comprises around 50wt% olefin. These C₄ cuts are fractionated at the outlet of the respective FCC or MTBE unit. The hydrocarbon feedstock may yet further comprise a C₄ cut from a naphtha steam-cracking unit of a petrochemical plant in which naphtha, comprising C₅ to C₉ species having a boiling point range of from about 15 to 180°C, is steam cracked to produce, *inter alia*, a C₄ cut. Such a C₄ cut typically comprises, by weight, 40 to 50% 1,3-butadiene, around 25% isobutylene, around 15% butene (in the form of but-1-ene and/or but-2-ene) and around 10% n-butane and/or isobutane. The olefin-containing hydrocarbon feedstock may also comprise a C₄ cut from a steam cracking unit after butadiene extraction (raffinate 1), or after butadiene hydrogenation.

The feedstock may yet further alternatively comprise a hydrogenated butadiene-rich C₄ cut, typically containing greater than 50wt% C₄ as an olefin. Alternatively, the hydrocarbon feedstock could comprise a pure olefin feedstock which has been produced in a petrochemical plant.

The olefin-containing feedstock may yet further alternatively comprise light cracked naphtha (LCN) (otherwise known as light catalytic cracked spirit (LCCS)) or a C₅ cut from a steam cracker or light cracked naphtha, the light cracked naphtha being fractionated from the effluent of the FCC unit, discussed hereinabove, in a crude oil refinery. Both such feedstocks contain olefins. The olefin-containing feedstock may yet further alternatively comprise a medium cracked naphtha from such an FCC unit or visbroken naphtha obtained from a visbreaking

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unit for treating the residue of a vacuum distillation unit in a crude oil refinery.

The olefin-containing feedstock may comprise a mixture of one or more of the above-described feedstocks.

The use of a C_5 cut as the olefin-containing hydrocarbon feedstock in accordance with a preferred process of the invention has particular advantages because of the need to remove C_5 species in any event from gasolines produced by the oil refinery. This is because the presence of C_5 in gasoline increases the ozone potential and thus the photochemical activity of the resulting gasoline. In the case of the use of light cracked naphtha as the olefin-containing feedstock, the olefin content of the remaining gasoline fraction is reduced, thereby reducing the vapour pressure and also the photochemical activity of the gasoline.

When converting light cracked naphtha, C_2 to C_4 olefins may be produced in accordance with the process of the invention. The C_4 fraction is very rich in olefins, especially in isobutene, which is an interesting feed for an MTBE unit. When converting a C_4 cut, C_2 to C_3 olefins are produced on the one hand and C_5 to C_6 olefins containing mainly iso-olefins are produced on the other hand. The remaining C_4 cut is enriched in butanes, especially in isobutane which is an interesting feedstock for an alkylation unit of an oil refinery wherein an alkylate for use in gasoline is produced from a mixture of C_3 and C_5 feedstocks. The C_5 to C_6 cut containing mainly iso-olefins is an interesting feed for the production of tertiary amyl methyl ether (TAME).

Surprisingly, the present inventors have found that in accordance with the process of the invention, olefinic feedstocks can be cracked selectively so as to redistribute the olefinic content of the feedstock in the resultant effluent. The catalyst and process conditions are selected whereby the process has a particular yield on an olefin basis towards a specified olefin

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in the feedstocks. Typically, the catalyst and process conditions are chosen whereby the process has the same high yield on an olefin basis towards propylene irrespective of the origin of the olefinic feedstocks for example the C_4 cut from the FCC unit, the C_4 cut from the MTBE unit, the light cracked naphtha or the C_5 cut from the light crack naphtha, etc., This is quite unexpected on the basis of the prior art. The propylene yield on an olefin basis is typically from 30 to 50% based on the olefin content of the feedstock. The yield on an olefin basis of a particular olefin is defined as the weight of that olefin in the effluent divided by the initial total olefin content by weight. For example, for a feedstock with 50wt% olefin, if the effluent contains 20wt% propylene, the propylene yield on an olefin basis is 40%. This may be contrasted with the actual yield for a product which is defined as the weight amount of the product produced divided by the weight amount of the feed. The paraffins and the aromatics contained in the feedstock are only slightly converted in accordance with the preferred aspects of the invention.

In accordance with preferred aspects of the present invention, the catalyst for the cracking of the olefins comprises a crystalline silicate of the MFI family which may be a zeolite, a silicalite or any other silicate in that family.

The preferred crystalline silicates have pores or channels defined by ten oxygen rings and a high silicon/aluminium atomic ratio.

Crystalline silicates are microporous crystalline inorganic polymers based on a framework of XO_4 tetrahedra linked to each other by sharing of oxygen ions, where X may be trivalent (e.g. Al, B, ...) or tetravalent (e.g. Ge, Si, ...). The crystal structure of a crystalline silicate is defined by the specific order in which a network of tetrahedral units are linked together. The size of the crystalline silicate pore openings is determined by the number of tetrahedral units, or, alternatively,

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oxygen atoms, required to form the pores and the nature of the cations that are present in the pores. They possess a unique combination of the following properties: high internal surface area; uniform pores with one or more discrete sizes; ion exchangeability; good thermal stability; and ability to adsorb organic compounds. Since the pores of these crystalline silicates are similar in size to many organic molecules of practical interest, they control the ingress and egress of reactants and products, resulting in particular selectivity in catalytic reactions. Crystalline silicates with the MFI structure possess a bidirectional intersecting pore system with the following pore diameters: a straight channel along [010]: 0.53-0.56 nm and a sinusoidal channel along [100]: 0.51-0.55 nm.

The crystalline silicate catalyst has structural and chemical properties and is employed under particular reaction conditions whereby the catalytic cracking readily proceeds. Different reaction pathways can occur on the catalyst. Under the process conditions, having an inlet temperature of around 500 to 600°C, preferably from 520 to 600°C, yet more preferably 540 to 580°C, and an olefin partial pressure of from 0.1 to 2 bars, most preferably around atmospheric pressure, the shift of the double bond of an olefin in the feedstock is readily achieved, leading to double bond isomerisation. Furthermore, such isomerisation tends to reach a thermodynamic equilibrium. Propylene can be, for example, directly produced by the catalytic cracking of hexene or a heavier olefinic feedstock. Olefinic catalytic cracking may be understood to comprise a process yielding shorter molecules via bond breakage.

The catalyst preferably has a high silicon/aluminium atomic ratio, greater than about 300, whereby the catalyst has relatively low acidity. Hydrogen transfer reactions are directly related to the strength and density of the acid sites on the catalyst, and such reactions are preferably suppressed so as to avoid the formation of coke during the olefin conversion process,

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which in turn would otherwise decrease the stability of the catalyst over time. Such hydrogen transfer reactions tend to produce saturates such as paraffins, intermediate unstable dienes and cyclo-olefins, and aromatics, none of which favours cracking into light olefins. Cyclo-olefins are precursors of aromatics and coke-like molecules, especially in the presence of solid acids, i.e. an acidic solid catalyst. The acidity of the catalyst can be determined by the amount of residual ammonia on the catalyst following contact of the catalyst with ammonia which adsorbs to the acid sites on the catalyst with subsequent ammonium desorption at elevated temperature measured by differential thermogravimetric analysis. Preferably, the silicon/aluminium ratio ranges from 300 to 1000, most preferably from 300 to 500.

One of the features of the invention is that with such high silicon/aluminium ratio in the crystalline silicate catalyst, a stable olefin conversion can be achieved with a high propylene yield on an olefin basis of from 30 to 50% whatever the origin and composition of the olefinic feedstock. Such high ratios reduce the acidity of the catalyst, thereby increasing the stability of the catalyst.

Not only is it required in accordance with the present invention to achieve a high propylene yield on an olefin basis, but also it is required to achieve a high purity of propylene in the C₃ species in the effluent in conjunction with a high percentage of the olefins in the feedstock being cracked into olefins, rather than being cracked into paraffin or aromatic compounds. Preferably, the propylene has a purity of at least 93%. Preferably, at least 85% by weight of the olefins in the feedstock are cracked into olefins or are present as the initial olefin. In addition, it is also preferred in accordance with the invention for the catalyst to have high stability in the cracking process in the sense that the catalyst is not reduced in activity as a result of coke being progressively deposited or formed on the catalyst. Such coke formation has been found by

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the inventors to lead to a significant decrease of the ability of the catalyst to crack the olefins with a high propylene yield over time. All of these desired results in the cracking process may be achieved in accordance with the invention by providing a silicon/aluminium atomic ratio in the crystalline silicate catalyst of the MFI-type of at least about 300, in conjunction with the required process parameters of temperature and pressure.

The various preferred catalysts of the present invention have been found to exhibit high stability, in particular being capable of giving a stable propylene yield over several days, e.g. up to ten days. This enables the olefin cracking process to be performed continuously in two parallel "swing" reactors wherein when one reactor is operating, the other reactor is undergoing catalyst regeneration. The catalyst of the present invention also can be regenerated several times. The catalyst is also flexible in that it can be employed to crack a variety of feedstocks, either pure or mixtures, coming from different sources in the oil refinery or petrochemical plant and having different compositions.

In the catalytic cracking process, the process conditions are selected in order to provide high selectivity towards propylene, a stable olefin conversion over time, and a stable olefinic product distribution in the effluent. Such objectives are favoured by the use of a low acid density in the catalyst (i.e. a high Si/Al atomic ratio) in conjunction with a low pressure, a high inlet temperature and a short contact time, all of which process parameters are interrelated and provide an overall cumulative effect (e.g. a higher pressure may be offset or compensated by a yet higher inlet temperature). The process conditions are selected to disfavour hydrogen transfer reactions leading to the formation of paraffins, aromatics and coke precursors. The process operating conditions thus employ a high space velocity, a low pressure and a high reaction temperature. Preferably, the LHSV ranges from 10 to 30h^{-1} . The olefin partial pressure ranges from 0.1 to 2 bars, more preferably from 0.5 to

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1.5 bars. A particularly preferred olefin partial pressure is atmospheric pressure (i.e. 1 bar). The hydrocarbon feedstocks are preferably fed at a total inlet pressure sufficient to convey the feedstocks through the reactor. The hydrocarbon feedstocks may be fed undiluted or diluted in an inert gas, e.g. nitrogen. Preferably, the total absolute pressure in the reactor ranges from 0.5 to 10 bars. The present inventors have found that the use of a low olefin partial pressure, for example atmospheric pressure, tends to lower the incidence of hydrogen transfer reactions in the cracking process, which in turn reduces the potential for coke formation which tends to reduce catalyst stability. The cracking of the olefins is performed at an inlet temperature of the feedstock of from 500 to 600°C, more preferably from 520 to 600°C, yet more preferably from 540 to 580°C, typically around 560°C to 570°C.

The catalytic cracking process can be performed in a fixed bed reactor, a moving bed reactor or a fluidized bed reactor. A typical fluid bed reactor is one of the FCC type used for fluidized-bed catalytic cracking in the oil refinery. A typical moving bed reactor is of the continuous catalytic reforming type. As described above, the process may be performed continuously using a pair of parallel "swing" reactors.

Since the catalyst exhibits high stability to olefinic conversion for an extended period, typically at least around ten days, the frequency of regeneration of the catalyst is low. More particularly, the catalyst may accordingly have a lifetime which exceeds one year.

After the catalytic cracking process, the reactor effluent is sent to a fractionator and the desired olefins are separated from the effluent. When the catalytic cracking process is employed to produce propylene, the C₃ cut, containing at least 93% propylene, is fractionated and thereafter purified in order to remove all the contaminants such as sulphur species, arsine, etc.. The heavier olefins of greater than C₃ can be recycled.

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In accordance with various aspects of the present invention, not only can a variety of different olefinic feedstocks be employed in the cracking process, but also, by appropriate selection of the process conditions and of the particular catalyst employed, the olefin conversion process can be controlled so as to produce selectively particular olefin distributions in the resultant effluents.

For example, in accordance with a primary aspect of the invention, olefin-rich streams from refinery or petrochemical plants are cracked into light olefins, in particular propylene. The light fractions of the effluent, namely the C₂ and C₃ cuts, can contain more than 95% olefins. Such cuts are sufficiently pure to constitute chemical grade olefin feedstocks. The present inventors have found that the propylene yield on an olefin basis in such a process can range from 30 to 50% based on the olefinic content of the feedstock which contains one or more olefins of C₄ or greater. In the process, the effluent has a different olefin distribution as compared to that of the feedstock, but substantially the same total olefin content.

In a further embodiment, the process of the present invention produces C₂ to C₃ olefins from a C₅ olefinic feedstock. The catalyst is of crystalline silicate having a silicon/aluminium ratio of at least 300, and the process conditions are an inlet temperature of from 500 to 600°C, an olefin partial pressure of from 0.1 to 2 bars, and an LHSV of 10 to 30h⁻¹, yielding an olefinic effluent having at least 40% of the olefin content present as C₂ to C₃ olefins.

Another preferred embodiment of the present invention provides a process for the production of C₂ to C₃ olefins from a light cracked naphtha. The light cracked naphtha is contacted with a catalyst of crystalline silicate having a silicon/aluminium ratio of at least 300, to produce by cracking an olefinic effluent wherein at least 40% of the olefin content is present as C₂ to C₃ olefins. In this process, the process

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conditions comprise an inlet temperature of 500 to 600°C, an olefin partial pressure of from 0.1 to 2 bars, and an LHSV of 10 to 30h⁻¹.

The various aspects of the present invention are illustrated below with reference to the following non-limiting Examples.

Example 1

In this Example, a feedstock comprising 1-hexene was fed through a reactor at an inlet temperature of around 580°C, an outlet hydrocarbon pressure of atmospheric pressure and an LHSV of around 25 h⁻¹ over ZSM-5 type catalysts available in commerce from the company CU Chemie Ueticon AG of Switzerland under the trade name ZEOCAT P2-2. The catalysts being commercially available had been prepared by crystallisation using an organic template and had been unsubjected to any subsequent steaming or de-alumination process. The catalysts had a varying silicon/aluminium atomic ratio of 50, 200, 300 and 490. The crystal size of each catalyst was from 2 to 5 microns and the pellet size was from 35 to 45 mesh. A number of runs were performed and for each run the composition of the effluent was examined to yield an indication of the sum of each of the olefins, saturates and aromatics in the effluent for various Si/Al atomic ratio values. The results obtained, after 5 hours on stream, of those runs are illustrated in Figure 1. Figure 1 shows the yield of propylene in the effluent, the percentage conversion of the 1-hexene olefinic feedstock following the olefinic catalytic cracking process of the invention and the sum of the saturates, olefins and aromatics in the effluent. The purity of the propylene, in terms of the amount of propylene in the C₃ species in the effluent, was 70%, 91%, 93% and 97% for the four runs of increasing Si/Al atomic ratio.

For silicon/aluminium atomic ratios in the commercial catalysts of from about 200 to 300, both the yield of olefins in the effluent and the yield of propylene on an olefin basis are

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lower than the desired values of 85% and 30% respectively. The propylene purity is also less than typical desired value commercially of 93%. This demonstrates the need for increasing the Si/Al atomic ratios of commercially available catalysts by steaming and de-alumination as described hereinabove and de-alumination as described hereinabove, typically to above 300. In contrast, when such steaming and de-alumination process are employed, the resultant Si/Al ratio is preferably greater than only 180 in order to obtain the desired olefin content in the effluent, propylene yield on an olefin basis, and purity of propylene. At an Si/Al atomic ratio of greater than about 300 in a commercially available catalyst which has not been pretreated by steaming and de-alumination, at least about 85% of the olefins in the feedstock are cracked into olefins or are present as the initial olefin. Thus at an Si/Al atomic ratio of greater than 300, the feedstock and the effluent have substantially the olefin content by weight therein, to the extent that the olefin content by weight of the feedstock and the effluent are within $\pm 15\text{wt}\%$ of each other. Moreover, at a Si/Al atomic ratio of at least about 300 in such a commercially available untreated catalyst, the yield of propylene is at least around 30% by weight on an olefin basis. At an Si/Al atomic ratio of around 490 in such a commercially available untreated catalyst, the olefin content of the effluent is greater than about 90% by weight of the olefin content of the feedstock and the propylene yield on an olefin basis approaches 40%.

Example 2

In this Example, a variety of different crystalline silicates of the MFI type having different silicon/aluminium atomic ratios were employed in the catalytic cracking of an olefin feedstock. The MFI silicates comprise zeolites of the ZSM-5 type, in particular zeolite sold in commerce under the trade name H-ZSM-5 available in commerce from the company PQ Corporation of Southpoint, P.O. Box 840, Valley Forge, PA 19482-0840, USA. The crystalline silicates had a particle size of from

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35-45 mesh and were not modified by prior treatment.

The crystalline silicates were loaded into a reactor tube and heated to a temperature of around 530°C. Thereafter, one gram of 1-hexene was injected into the reactor tube in a period of 60 seconds. The injection rate had a WHSV of 20h^{-1} and a catalyst to oil weight ratio of 3. The cracking process was performed at an outlet hydrocarbon pressure of 1 bar (atmospheric pressure).

Table 1 shows the yield in terms of wt% of various constituents in the resultant effluent and also the amount of coke produced on the catalyst in the reactor tube.

It may be seen that for crystalline silicates having a low Si/Al atomic ratio, a significant degree of coke is formed on the catalyst. This in turn would lead to a poor stability over time of the catalyst when used for a catalytic cracking process for olefins. In contrast, it may be seen that for the crystalline silicate catalyst having a high silicon/aluminium atomic ratio, and the example being around 350, no coke is produced on the catalyst, leading to high stability of the catalyst.

It may be seen that for the high Si/Al atomic ratio (350) catalyst, the propylene yield on an olefin basis is around 28.8 in the effluent, being significantly higher than the propylene yield of the two runs using the low Si/Al atomic ratios. It may be thus be seen that the use of a catalyst having a high silicon/aluminium atomic ratio increases the propylene yield on an olefin basis in the catalytic cracking of olefins to produce other olefins.

An increase in the Si/Al atomic ratio was also found to reduce the formation of propane.

Comparative Examples 1 & 2

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In these Comparative Examples, commercially available silicalite catalysts which had not been subjected to a steaming and de-alumination process by extraction were employed in the catalytic cracking of a feedstock comprising butene.

In the catalytic cracking process, the butene-containing feedstock had the composition as specified in Tables 2a and 2b.

The catalytic cracking process was carried out at an inlet temperature of 545°C, an outlet hydrocarbon pressure of atmospheric pressure and at an LSHV of 30h⁻¹.

Tables 2a and 2b show the breakdown of the propylene, iso-butene and n-butene amounts present in the effluent.

In Comparative Example 1 the catalyst comprised a silicalite having a silicon/aluminium ratio of around 120, and having a crystallite size of from 4 to 6 microns and a surface area (BET) of 399m²/g. The silicalite was pressed, washed and the 35-45 mesh fraction was retained. The catalyst had not been subjected to any steaming and alumination extraction process. In Comparative Example 2 the catalyst comprised the same starting silicalite as in Comparative Example 1 which had been subjected to a steaming process in an atmosphere of 72vol% steam and 28vol% nitrogen at a temperature of 550°C at atmospheric pressure for a period of 48 hours, but not an aluminium extraction process. The results are shown in Tables 2a and 2b respectively.

It may be seen that for Comparative Example 1 and Comparative Example 2 the catalyst did not exhibit stability. In other words, the catalyst reduced its ability over time to catalyse the cracking process. It is believed that this is because of the formation of coke on the catalyst, which in turn results from the use of a low silicon/aluminium atomic ratio in the catalyst, leading to a relatively high acidity for the catalyst.

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For Comparative Example 1, there was also a significant formation of paraffins, e.g. propane.

Example 3

In this Example, a feedstock comprising a 1-butene feed having the composition as specified in Table 3 was fed through a reactor at an inlet temperature of around 560°C, an outlet hydrocarbon pressure of atmospheric pressure and an LHSV of around 23h⁻¹ over the same catalyst employed in Example 1. The catalyst had a silicon/aluminium atomic ratio of 300, as for one of the catalysts employed in Example 1. The catalyst was commercially available, as for Example 1 and had been prepared by crystallisation using an organic template and had been unsubjected to any subsequent steaming or de-alumination process. The crystal size of each catalyst and the pellet size were as specified for Example 1. The composition of the effluent was examined after 40 hours on stream and after 112 hours on stream and the results of the analysis of the effluent are indicated in Table 3. Table 3 shows that the catalyst having a silicon/aluminium atomic ratio of 300 has great stability with respect to the catalytic cracking process which is selective to propylene in the effluent. Thus after 40 hours on stream the propylene comprised 18.32 wt% in the effluent whereas after 112 hours on stream the propylene comprised 18.19 wt% of the effluent. After 162 hours on stream the propylene comprised 17.89wt% of the effluent. This shows that the propylene content in the effluent does not significantly reduce over quite significant periods of time of up to about 5 days, and more than 3 days. A period of 3 days is typically a recycling or regeneration period employed for two parallel "swing" reactors of the fixed bed type. The results of Example 3 after the periods of 112 hours and 162 hours may be respectively compared to those of Comparative Example 1 after the periods of 97 hours and 169 hours. For Comparative Example 1 the catalyst was reasonably stable over 97 hours, with a decrease in the propylene content in the effluent of around 1.1% as compared to the initial

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volume, but the stability decreased significantly between 97 hours and 169 hours, which is not the case for the corresponding periods of 112 hours and 162 hours for Example 3.

Comparative Example 3

In this Comparative Example, a commercially available ZSM-5 catalyst having a silicon/aluminium atomic ratio of 25 was employed in the catalytic cracking of a feedstock comprising butene. In the catalytic cracking process, the butene-containing feedstock had the composition as specified in Table 4.

The catalytic cracking process was carried out at an inlet temperature of 560°C, an outlet hydrocarbon pressure of atmospheric pressure and an LHSV of 50h⁻¹.

The catalyst and the process conditions, in particular the high space velocity, were selected so as to simulate the corresponding catalyst and conditions disclosed in EP-A-0109059 referred to hereinabove.

The catalytic cracking process was performed for a period of nearly 40 hours and periodically the composition of the effluent was determined after successive periods of time on stream (TOS). The composition of the effluent, with a corresponding indication of the degree of conversion of the butenes, after particular times on stream are specified in Table 4.

It may be seen from Table 4 that when a ZSM-5 catalyst having a low silicon/aluminum atomic ratio of around 25 is employed in conjunction with high space velocities, which EP-A-0109059 indicates as being important for achieving high propylene yield, then although the propylene yield may be sufficiently high to yield around 16wt% propylene in the effluent, this occurs after a period of around 15-20 hours on stream and after that period the propylene yield rapidly deteriorates. This indicates

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low catalyst stability with the use of a low silicon/aluminium atomic ratio in conjunction with a high space velocity as employed in the processes disclosed in EP-A-0109059.

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TABLE 1

	Yield/wt%			
	Propane	Propylene	Gas#	Coke
H-ZSM-5 [25]	28	5.8	59.3	4.35
H-ZSM-5 [40]	19.8	10	60.4	1.44
H-ZSM-5 [350]	1.8	28.8	63.8	0

#gas = H₂, C₂ to C₄ olefins and paraffins

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TABLE 2a

Comparative Example 1

Silicalite non-modified (Si/Al=120)

T in (°C) 549

LHSV (h⁻¹) 30

TOS (h)			5	97	169
			Feed	Effluent	Effluent
Conversion of n-butenes (%)			85.20	79.90	55.90
C ₁	P1	0.00	0.41	0.21	0.10
	P2	0.00	0.51	0.17	0.00
C ₂	O2	0.00	8.64	4.97	0.90
	P3	0.30	3.80	1.61	0.40
C ₃	O3	0.10	20.36	19.25	8.48
	iP4	31.10	31.57	29.92	30.71
C ₄	nP4	12.80	13.27	13.03	13.06
	iO4	3.70	5.14	6.70	13.46
	nO4	51.00	7.76	9.96	22.43
C ₅	iP5+nP5+cP5	0.00	0.93	1.19	0.50
	iO5+nO5+cO5	0.20	4.11	6.69	6.98
C ₆	C6+	0.80	3.50	6.30	2.99
Total			100.00	100.00	100.00
Olefins O ₂ -O ₅			55.00	46.01	47.57
Paraffins P ₁ -P ₅			44.20	50.49	46.13
Others & Unknown			0.80	3.50	6.30
Total			100.00	100.00	100.00

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TABLE 2b

Comparative Example 2

Silicalite steamed

T in (°C) 549

LHSV (h⁻¹) 29.6

TOS(h)			16	72
		Feed	Effluent	Effluent
Conversion of n-butenes			73.10	70.10
C ₁	P1	0.00	0.20	0.10
C ₂	P2	0.00	0.10	0.00
	O2	0.00	2.73	1.71
C ₃	P3	0.10	0.40	0.30
	O3	0.30	17.89	14.27
C ₄	iP4	33.40	33.87	33.16
	nP4	9.70	10.11	10.15
	iO4	2.40	10.11	10.75
	nO4	53.20	14.47	15.99
C ₅	iP5+nP5+cP5	0.50	0.51	0.50
	iO5+nO5+cO5	0.10	7.18	8.54
C ₆	C6+	0.30	2.43	4.52
Total		100.00	100.00	100.00
Olefins	O ₂ -O ₅	56.00	52.38	51.26
Paraffins	P ₁ -P ₅	43.70	45.19	44.22
Others & Unknown		0.30	2.43	4.52
Total		100.00	100.00	100.00

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TABLE 3Example 3

Silicalite (Si/Al=300)

T In (°C) 560

LHSV (h⁻¹) 23

TOS (h)			40	112	162	
			Feed	Effluent	Effluent	Effluent
Conversion of n-butenes(%)			82.01	79.94	77.54	
C ₁	P1	0.01	0.31	0.25	0.20	
C ₂	P2	0.00	0.41	0.33	0.27	
	O2	0.00	5.51	4.81	4.14	
C ₃	P3	0.22	2.02	1.54	1.23	
	O3	0.06	18.32	18.19	17.89	
	D3	0.01	0.00	0.00	0.00	
C ₄	iP4	29.40	29.26	28.45	28.15	
	nP4	15.41	15.76	16.40	16.35	
	iO4	2.55	6.03	6.80	7.51	
	nO4	52.15	9.38	10.46	11.72	
	D4	0.03	0.09	0.09	0.10	
C ₅	iP5	0.07	0.40	0.34	0.31	
	nP5	0.00	0.21	0.18	0.15	
	cP5	0.00	0.41	0.35	0.30	
	iO5	0.09	3.31	3.65	4.01	
	nO5	0.00	1.73	1.89	2.06	
	cO5	0.00	0.20	0.20	0.20	
	D5	0.00	0.14	0.14	0.13	
C ₆	iP6	0.00	0.04	0.03	0.02	
	nP6	0.00	0.06	0.05	0.05	
	cP6	0.00	0.43	0.34	0.27	

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	iO6	0.00	0.73	0.73	0.72
	nO6	0.01	1.50	1.37	1.24
	cO6	0.00	0.06	0.06	0.06
	D6	0.00	0.00	0.00	0.00
	A6	0.00	0.61	0.59	0.57
C ₇	iP7	0.00	0.07	0.06	0.05
	nP7	0.00	0.00	0.00	0.00
	cP7	0.00	0.21	0.18	0.14
	iO7	0.00	0.17	0.20	0.19
	nO7	0.00	0.08	0.08	0.07
	cO7	0.00	0.33	0.23	0.19
	D7	0.00	0.00	0.00	0.00
	A7	0.00	1.06	0.94	0.77
C ₈	iP8	0.00	0.09	0.09	0.09
	nP8	0.00	0.00	0.00	0.00
	cP8	0.00	0.03	0.01	0.01
	iO8	0.00	0.00	0.00	0.00
	nO8	0.00	0.00	0.00	0.00
	cO8	0.00	0.00	0.00	0.00
	A8	0.00	1.03	0.95	0.83
Total		100.00	100.00	100.00	100.00
Paraffins (P)		45.10	49.70	48.60	47.59
Olefins (O)		54.86	47.37	48.68	50.00
Dienes (D)		0.04	0.23	0.23	0.24
Aromatics (A)		0.00	2.70	2.49	2.17
Total		100.00	100.00	100.00	100.00

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TABLE 4Comparative Example 3

ZSM5 (Si/Al=25)

T in (°C) 560

LHSV(h-1) 50

TOS(h)			0.22	4.35	9.50	14.67	20.80	26.88	32.05	39.98
Feed			Effluent	Effluent	Effluent	Effluent	Effluent	Effluent	Effluent	Effluent
Conversion of butenes			93.59	88.88	82.58	76.71	67.29	55.85	43.02	28.04
C ₁	P1	0.02	3.69	2.02	0.85	0.34	0.17	0.12	0.09	0.06
	C ₂	0.00	5.48	2.23	0.94	0.52	0.23	0.12	0.07	0.03
C ₂	O2	0.00	4.29	6.26	6.92	5.32	3.36	1.88	1.07	0.37
	P3	0.34	28.07	16.97	9.22	3.64	1.65	0.98	0.62	0.55
C ₃	O3	0.12	6.05	9.36	12.81	15.99	16.04	13.09	10.03	5.48
	D3	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C ₄	iP4	32.04	12.31	23.44	26.54	33.90	33.72	33.84	32.22	33.72
	nP4	12.65	6.25	10.52	13.69	13.58	13.89	13.82	13.99	13.51
C ₄	iO4	2.22	1.37	2.39	3.74	4.99	6.17	8.35	10.60	12.31
	nO4	52.16	2.11	3.66	5.74	7.67	11.62	15.65	20.39	26.82
C ₅	D4	0.05	0.03	0.06	0.09	0.11	0.10	0.04	0.05	0.06
	iP5	0.25	0.87	1.10	1.11	0.59	0.44	0.34	0.34	0.23
C ₅	nP5	0.00	0.39	0.56	0.54	0.31	0.18	0.10	0.06	0.02
	cP5	0.00	0.12	0.24	0.39	0.31	0.19	0.10	0.05	0.01
C ₅	iO5	0.12	0.62	1.17	2.08	2.89	4.19	4.87	4.81	3.29
	nO5	0.01	0.32	0.61	1.09	1.50	2.17	2.53	2.51	1.73
C ₅	cO5	0.00	0.05	0.07	0.11	0.13	0.15	0.12	0.09	0.05
	D5	0.00	0.04	0.05	0.07	0.08	0.10	0.11	0.13	0.13
C ₆	iP6	0.00	0.09	0.15	0.14	0.06	0.02	0.01	0.00	0.00
	nP6	0.00	0.04	0.07	0.09	0.04	0.06	0.04	0.02	0.01
C ₆	cP6	0.00	0.11	0.24	0.46	0.35	0.15	0.06	0.03	0.01
	iO6	0.00	0.13	0.26	0.53	0.78	0.87	0.62	0.42	0.19
C ₆	nO6	0.01	5.05	3.93	3.06	1.98	1.44	1.12	0.93	0.66
	cO6	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.05	0.03
C ₆	D6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	A6	0.00	4.37	2.31	1.28	0.59	0.46	0.41	0.35	0.20
C ₇	iP7	0.00	0.03	0.06	0.08	0.08	0.07	0.06	0.04	0.02
	nP7	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00

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	cP7	0.00	0.03	0.09	0.19	0.18	0.11	0.06	0.03	0.01
	iO7	0.00	0.01	0.05	0.14	0.22	0.30	0.30	0.26	0.14
	nO7	0.00	0.01	0.02	0.06	0.08	0.11	0.11	0.10	0.06
	cO7	0.00	0.03	0.10	0.21	0.30	0.33	0.25	0.17	0.09
	D7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	A7	0.00	11.10	6.83	4.15	1.72	0.79	0.38	0.21	0.06
C ₈	iP8	0.00	0.01	0.01	0.03	0.05	0.07	0.07	0.08	0.04
	nP8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	cP8	0.00	0.00	0.01	0.02	0.02	0.02	0.02	0.02	0.02
	iO8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	nO8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	cO8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	A8	0.00	6.88	5.12	3.58	1.63	0.77	0.38	0.21	0.07
	Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	Paraffins	45.29	57.53	57.72	54.31	53.99	50.97	49.72	47.65	48.25
	Olefins	54.64	20.05	27.90	36.52	41.88	46.81	48.95	51.41	51.23
	Dienes	0.07	0.07	0.11	0.16	0.19	0.20	0.15	0.17	0.19
	Aromatics	0.00	22.35	14.26	9.01	3.94	2.02	1.17	0.76	0.33
	Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Paraffins = P

Olefins = O

Dienes = D

Aromatics = A

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CLAIMS:

1. A process for the catalytic cracking of an olefin-rich feedstock which is selective towards light olefins in the effluent, the process comprising contacting a hydrocarbon feedstock containing one or more olefins, with a MFI-type crystalline silicate catalyst having a silicon/aluminium atomic ratio of at least about 300 at an inlet temperature of from 500 to 600°C, at an olefin partial pressure of from 0.1 to 2 bars and the feedstock being passed over the catalyst at an LHSV of from 10 to 30h⁻¹, to produce an effluent with an olefin content of lower molecular weight than that of the feedstock.
2. A process according to claim 1, wherein the catalyst has been prepared by crystallisation using an organic template and has been unsubjected to any subsequent steaming or de-alumination process.
3. A process according to claim 2, wherein the catalyst comprises a ZSM-5 type catalyst.
4. A process according to any foregoing claim, wherein the silicon/aluminium atomic ratio is from 300 to 1000.
5. A process according to any foregoing claim, wherein the feedstock comprises C₄ to C₁₀ hydrocarbons.
6. A process according to any foregoing claim, wherein the effluent is rich in propylene.
7. A process according to claim 6, wherein propylene comprises at least 93% of the C₃ compounds present in the effluent.
8. A process according to claim 6 or claim 7, wherein the catalytic cracking has a propylene yield on an olefinic basis of from 30 to 50% based on the olefin content of the feedstock.

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9. A process according to any foregoing claim, wherein the olefin contents by weight of the feedstock and of the effluent are within $\pm 15\%$ of each other.

10. A process according to any foregoing claim, wherein the inlet temperature is from 540 to 580°C.

FIGURE 1

